

SYMPOSIUM ON PYROLYSIS REACTIONS OF FOSSIL FUELS
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USE OF THE LASER-MICROPYROLYSIS-MASS SPECTROMETER
IN STUDYING THE PYROLYSIS OF COAL

By

F. J. Vastola and A. J. Pirone
Department of Fuel Science
Penn State University
University Park, Pennsylvania

INTRODUCTION

The study of the pyrolysis products of high molecular weight organic materials has been a fruitful method of determining their structure. The structural identification becomes more difficult if the pyrolysis products undergo secondary reaction and consequently are not representative of the original structure. In order to minimize secondary reactions the following experimental criteria should be satisfied. To minimize reaction within the solid the heating rate should be high and its duration short. Surface rather than bulk heating would also be advantageous. To minimize gas phase interactions the pyrolysis should take place in vacuo. To insure analysis of materials of low vapor pressure and of free radicals the analysis should take place within one mean free path of the pyrolysis zone. Also, since coal is a highly heterogeneous material the analytical system has to have high sensitivity due to the inherent difficulty in separating large quantities of selected petrographic constituents.

Mass spectrometric techniques of analysis present themselves as a method of satisfying many of the above criteria. Coal (1, 2, 3), as well as coal extracts (4, 5), have been pyrolyzed in mass spectrometers and stable pyrolysis products and coal derivatives have been studied using heated inlet systems (6, 7, 8). However, none of the above techniques have met the requirements of rapid heating and minimum contact of the pyrolysis products with the bulk material.

The development of the laser has made available a compact source that can provide controlled heating fluxes of 10^6 cal./sec./cm.². Focused lasers have been used to vaporize graphite in mass spectrometer sources. (9, 10) The laser has been used also to pyrolyze coal with subsequent analysis of the permanent gaseous decomposition products. (11) Coal because of its low reflectivity is an ideal material to heat by focused laser radiation. When coal is heated by a focused laser beam only a few nanograms are pyrolyzed, but this is a sufficient quantity for analysis if the products are released within the ionization chamber of a mass spectrometer. Since the pyrolysis time is short (ca. 0.4 millisecond) only a time-of-flight mass spectrometer can be used to produce a complete spectrum of a pyrolysis from a single flash. In this type of instrument ions are produced in pulses, accelerated and resolved according to their time of flight down a field free drift tube to a detector. A complete mass spectrum can be recorded for a single pulse of ions. Since the ion pulse width is of the order of 5 microseconds, several spectra can be recorded during the pyrolysis.

If the coal to be pyrolyzed is viewed through the same optical system that is used to focus the laser output the area to be heated can be selected. This capability enables the petrographic constituents of coal to be pyrolyzed in-situ.

EXPERIMENTAL

Figure 1 shows a picture of the complete laser-mass spectrometer. Figure 2 shows a more detailed view of the laser and its microscope optics. Figure 3 is a schematic representation of the laser, ionization chamber and inlet system of the instrument.

The high coherency and low divergence of the light output of a pulsed ruby-laser greatly simplify the design of the optical system needed to produce small areas of intense illumination. A simple lens can concentrate the laser output sufficiently to vaporize carbon. In this application we are faced with two conflicting requirements; in order to achieve maximum light concentration a lens of short focal length is desired, however, in order to obtain a large working distance (lens to target distance) a lens of long focal length is needed. A compromise was made by using a 2X objective lens (Leitz VO) which gave working distance of 75 mm.

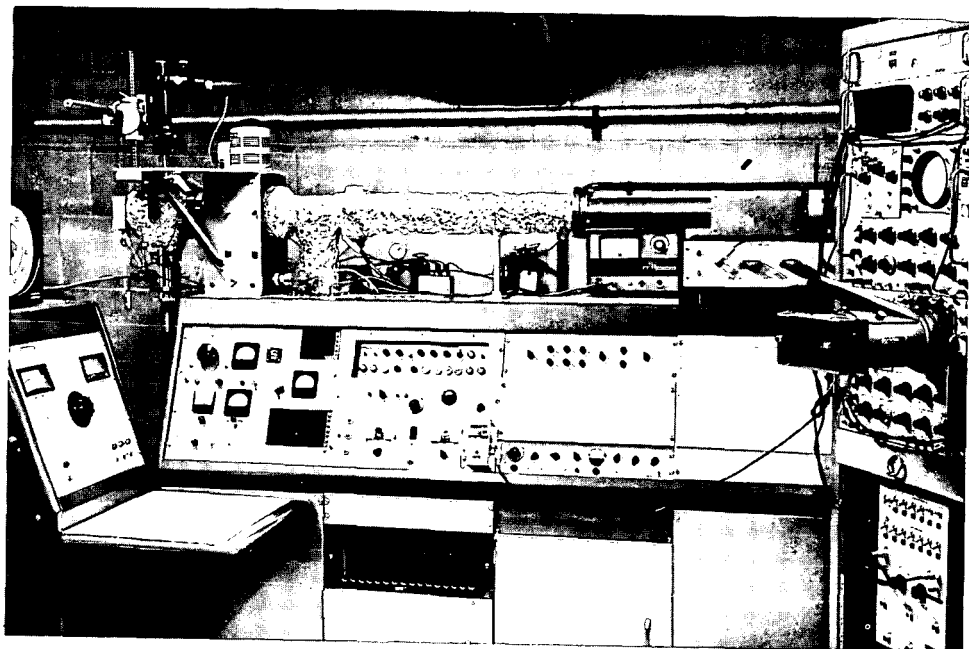


FIGURE 1 - LASER-MASS SPECTROMETER

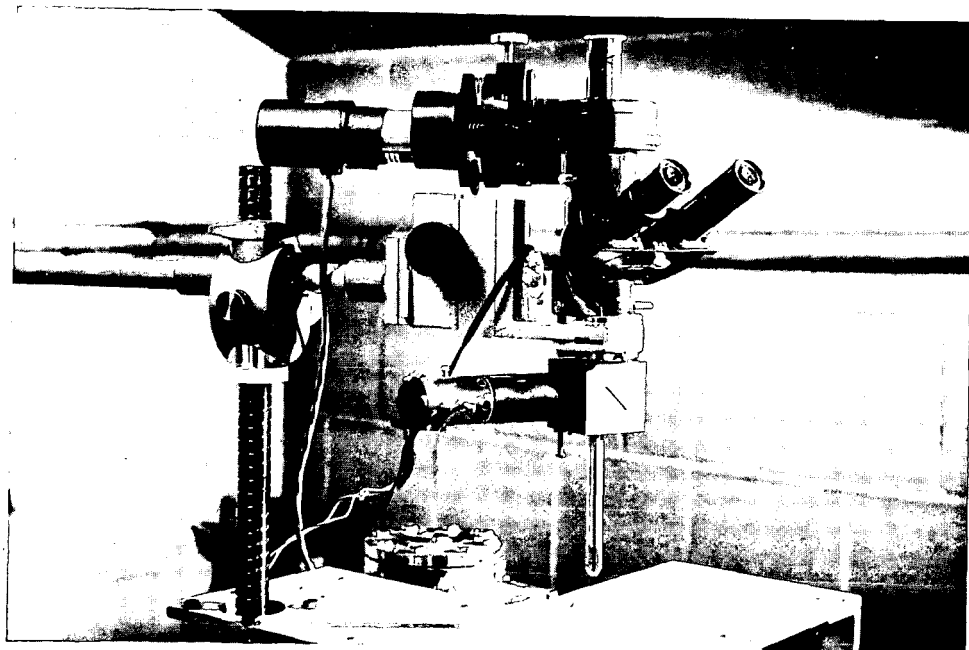


FIGURE 2 - LASER-MICROSCOPE ASSEMBLY

The Laser head consists of a T.R.G., Inc., Model 103, Minilaser and Model 153 microscope coupling. The laser is a 6.35 x 38 mm. ruby rod pumped by a helical gas discharge lamp. When the laser is pumped by a 230 joule discharge its output is 100 millijoules. The output pulse length is 0.4 to 0.5 milliseconds in duration. The wavelength of the laser light is 6943Å. The laser concentration and viewing system is constructed around a Leitz binocular-monocular FS microscope head.

The 25 X eye pieces (Leitz periplanatic wide field) in conjunction with the 2X objective give a total magnification of 50 X. The high power eye piece in conjunction with the low power objective degrades image resolution but this solution was necessary due to the problem of working distance mentioned above. However, image quality is sufficient to locate the desired pyrolysis areas. The target is illuminated for viewing by a vertical illuminator. The reflecting surface of the illuminator is a microscope slide mounted permanently in the optical path at an angle of 45 degrees. In order to minimize clearance problems the objective lense was mounted at the end of a 86 by 12 mm. extension tube. The entire optical system is mounted outside of the vacuum system. The flange above the in source in the Bendix model 12-107 TOF mass spectrometer has a 25 by 100 mm. well with an optical flat window at its lower surface. The objective lense can be lowered down this well to reach its proper working distance.

The polished coal sample (12 by 3 mm. surface) is mounted in a positioning clamp and inserted into the mass spectrometer through a modified Bendix model 843A direct inlet port. In position the coal sample is located just underneath the electron beam in the mass spectrometer ionizing chamber.

Figure 4 is a block diagram showing the electrical interconnection of the various units of the spectrometer system. Figure 5 shows the timing of the operating sequence. The master clock (Tektronix Model 180-S1) provides 10Kc. synchronizing pulses as well as 200 and 1000 Kc. reference timing markers. The TOF spectrometer is set to run synchronously with the 10Kc. master clock. When the laser-fire switch is activated the first arriving 10Kc. pulse will fire the flash tube in the laser head and start the delay timer in the oscilloscope (Tektronix model RM45B with type CA preamplifier). At the end of the preset delay time, the spectra can be displayed representing the composition of the pyrolysis product cloud above the coal at various times, in 0.1 millisecond increments, after the laser is fired. This delay is necessary since it may take up to 0.2 milliseconds for the laser to reach its peak output. The single sweep can be adjusted to give a complete mass scan (1 to 2000 AM.U.) or a magnified presentation of a limited mass range. The spectra are recorded on Polaroid Polascope type 410 film. Figure 6 shows a series of craters produced by laser radiation and Figure 7 shows a typical spectrum.

RESULTS

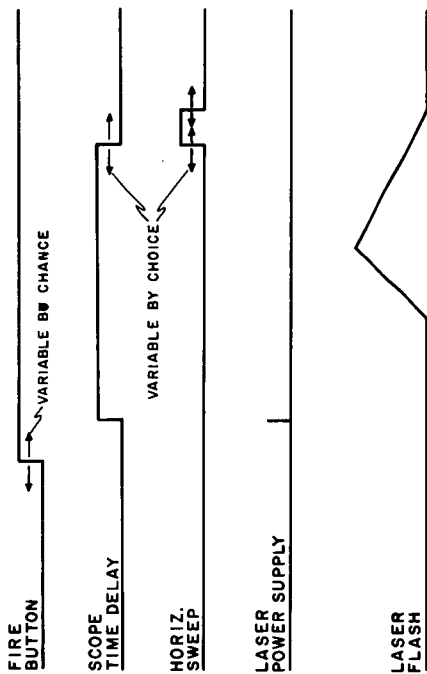
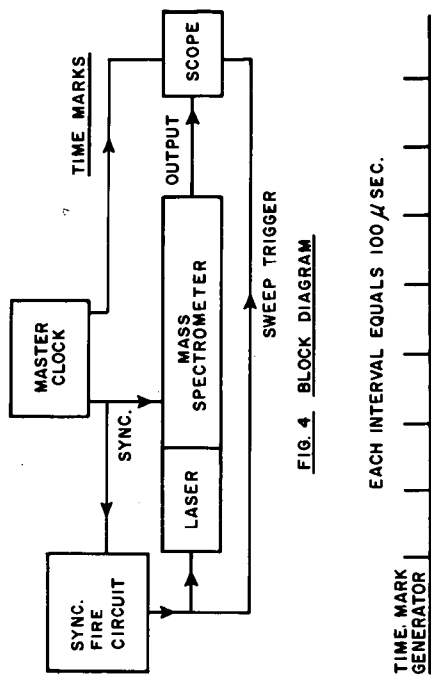
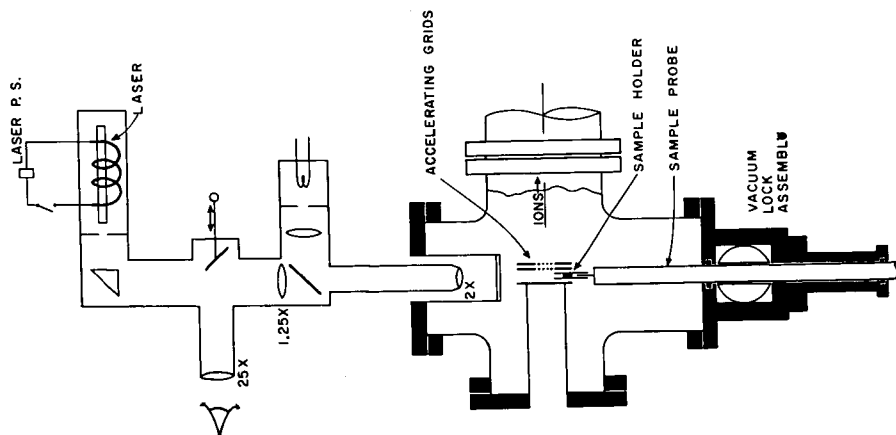
Figure 8 depicts an intermediate molecular weight portion of the pyrolysis products of a high volatile A, Pittsburgh seam bituminous coal.

The spectrum indicates the presence of both aromatic and aliphatic substituted aromatic compounds. Some of the possible assignments are given in Table I, only hydrocarbons are considered.

TABLE I
MASS ASSIGNMENTS

M/e	Ion	Compound
78	C ₆ H ₆ ⁺	Benzene
92	C ₇ H ₈ ⁺	Methylbenzene
106	C ₈ H ₁₀ ⁺	Dimethylbenzene, Ethylbenzene
128	C ₁₀ H ₈ ⁺	Naphthalene
142	C ₁₁ H ₁₀ ⁺	Methylnaphthalene
156	C ₁₂ H ₁₂ ⁺	Dimethylnaphthalene, Ethylnaphthalene

The spectrum in Figure 8 was obtained using an ionization potential of 50eV. The spectra produced by electron bombardment have characteristic fragmentation patterns, in the case of methylbenzene the major peaks will be at mass 92 (C₇H₈⁺) and mass 91 (C₇H₇⁺) with only minor peaks at mass 90 (C₇H₆⁺) and mass 89 (C₇H₅⁺). However, the spectrum produced by laser pyrolysis has major peaks at masses 89 and 90. The intensity of a single peak in a mass spectrum is the sum of the contributions of all species having fragments at that particular mass. For



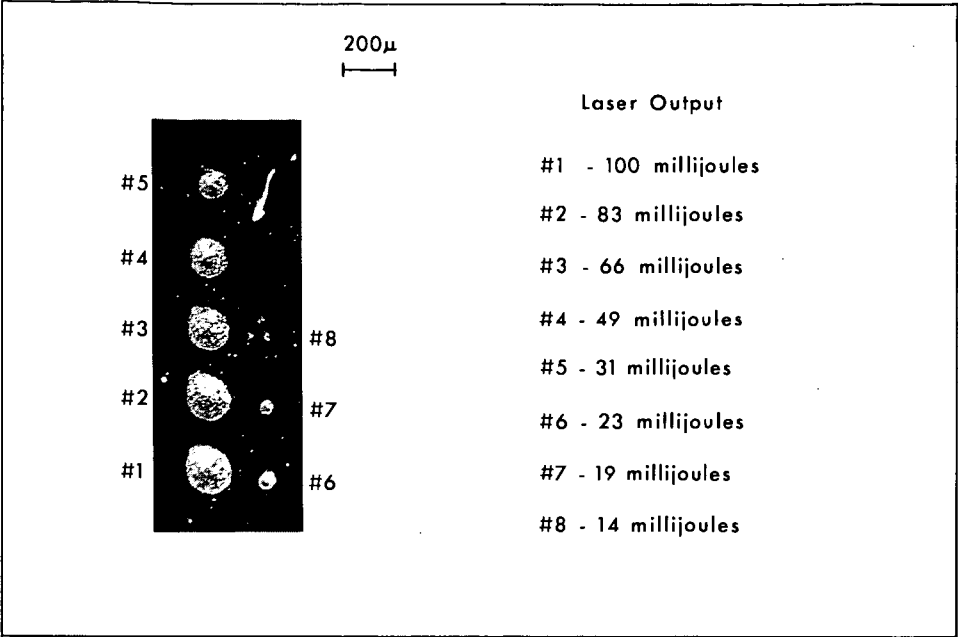


FIGURE 6 - LASER IRRADIATED COAL

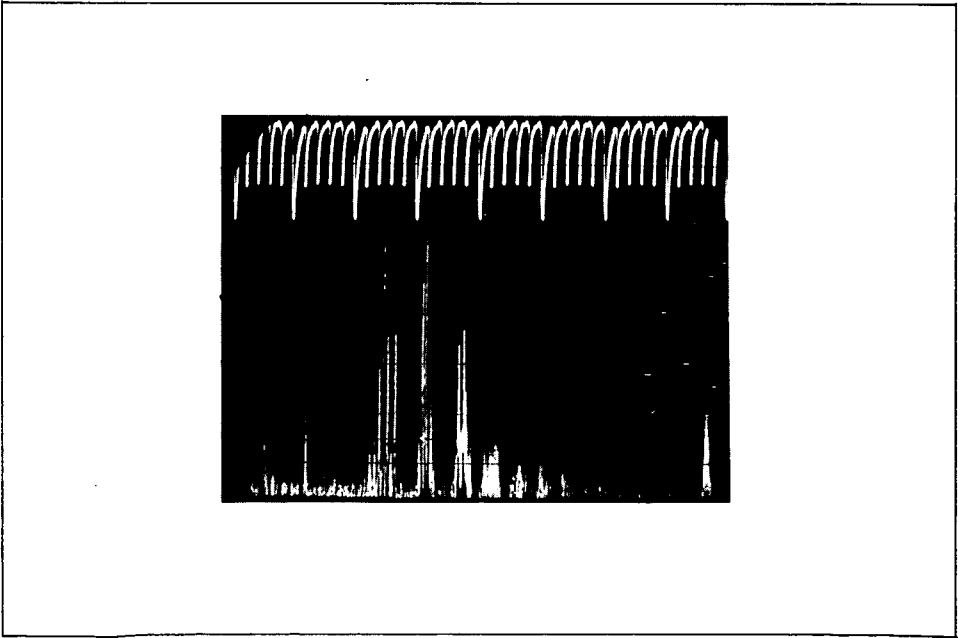


FIGURE 7 - A TYPICAL SPECTRUM

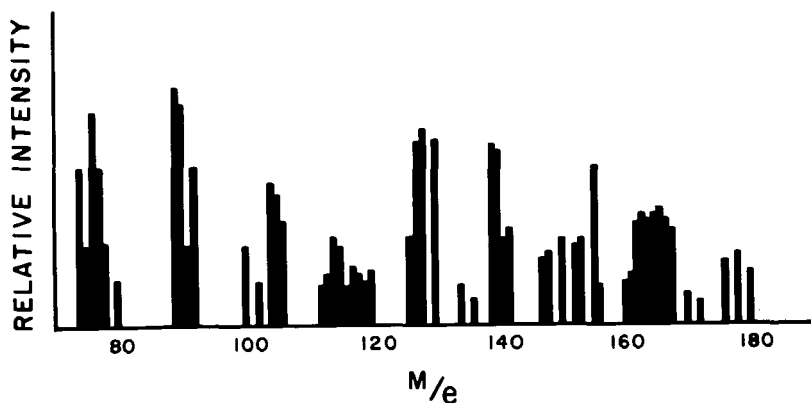


FIG. 8 SELECTED PORTION OF SPECTRA

example, the mass 91 ion is a major constituent of the spectra of other members of the aliphatic substituted series (e.g., dimethylbenzene, ethylbenzene). Since neither mass 89 or 90 is a major fragment in any hydrocarbon spectrum their presence indicates the existence of high concentrations of free radicals in the ionization chamber before electron bombardment. The same abnormal mass distribution, indicative of the existence of free radicals, is found in the benzene, naphthalene, methylnaphthalene and dimethylnaphthalene groupings of the mass spectrum. It therefore appears that the laser-mass spectrometer is capable of detecting primary coal pyrolysis products.

ACKNOWLEDGMENT

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